

X1: Perry's Chemical Engineer's Handbook, Sixth Edition, McGraw Hill International, 1984

13-58 DISTILLATION

wide-boiling components may not exhibit an azeotrope even though they form a very nonideal liquid mixture. Azeotropes occur infrequently for mixtures composed of components whose boiling points differ by more than 30°C (54°F).

An azeotrope is homogeneous if only one liquid phase is present. A maximum-boiling-point homogeneous azeotrope may occur if deviations from Raoult's law, as given by Eq. (13-10), are negative ($\gamma_i < 1.0$). For a minimum-boiling-point homogeneous azeotrope, deviations from Raoult's law are positive ($\gamma_i > 1.0$). If the positive deviations are large enough ($\gamma_i \gg 1.0$), phase splitting can occur and a minimum-boiling-point heterogeneous azeotrope may be formed with one vapor phase in equilibrium with two liquid phases. All three types of azeotropes are important. In some literature, mixtures that do not form azeotropes are called zeotropes.

An understanding of the occurrence of azeotropes is important for two reasons. First, azeotropes can make a given separation impossible by simple distillation in a particular pressure range. However, second, azeotropes may be utilized to separate mixtures not ordinarily separable by simple distillation or to increase recovery yield of some components from certain mixtures.

AZEOTROPIC-DISTILLATION PROCESSES

Azeotropic distillation refers to those processes in which a component (called the solvent or entrainer) is added above the main feed tray to form (or nearly form) with one or more of the feed components an azeotrope, which is removed as either the distillate or the bottoms, but usually the former. Azeotropic distillation can also refer to a process in which a solvent is added to break an azeotrope that otherwise would be formed by components in the feed. In this case, the process is distinguished from extractive distillation because the solvent appears in the distillate, from which it must be separated and recycled back to the top section of the column.

Representative processes for azeotropic distillation are shown in Figs. 13-61 and 13-62. Differences are due to the type of azeotrope formed and the method used to recover solvent. In Fig. 13-61, a mixture of cyclohexane [80.8°C (177.4°F)] and benzene [80.3°C (176.4°F)], which form a minimum-boiling homogeneous azeotrope [77.4°C (171.3°F)] and cannot be separated by simple distillation, is

*Figures in brackets are boiling points at 101.3 kPa (1 atm).

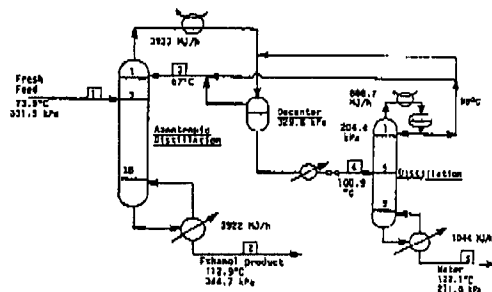


FIG. 13-62 Azeotropic-distillation process for separating ethanol and water by using pentane as the entrainer.

Material Balance, (kg-mol/h)

| Stream | 1 | 2 | 3 | 4 | 5 |
|-----------|--------|--------|--------|-------|-------|
| Ethanol | 32.555 | 32.555 | 13.138 | 2.500 | 0.000 |
| Water | 6.763 | 0.001 | 13.876 | 7.889 | 6.763 |
| n-Pentane | 0.000 | 0.000 | 07.532 | 0.000 | 0.000 |

fed to an azeotropic-distillation column together with acetone as an entrainer, which forms a minimum-boiling binary homogeneous azeotrope [58.1°C (127.6°F)] with acetone [56.4°C (133.5°F)]. Thus near-pure benzene is removed as bottoms. The acetone-cyclohexane near azeotrope is removed as distillate and is treated with water in a liquid-liquid extraction column, where near-pure cyclohexane leaves as overhead. An acetone-water mixture leaves the bottom of the extractor and is separated by simple distillation into separate solvent streams that are recycled. Thus, this process requires azeotropic distillation and two additional multistage separation operations.

Near-pure ethyl alcohol [78.3°C (172.9°F)] cannot be obtained from dilute mixtures with water [100°C (212°F)] by simple distillation at 101.3 kPa (1 atm) because a minimum-boiling homogeneous

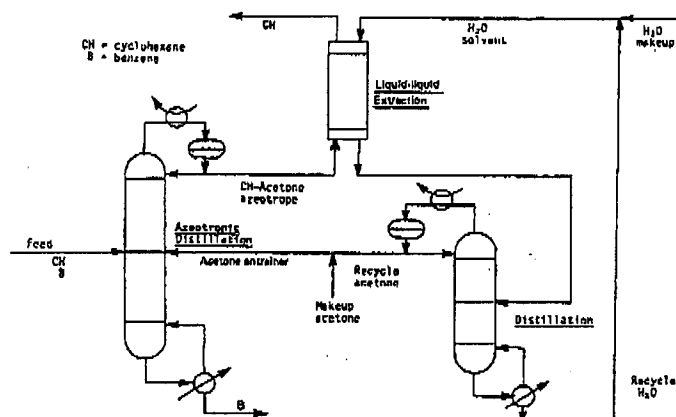


FIG. 13-61 Azeotropic-distillation process for separating cyclohexane from benzene by using acetone as the entrainer.